

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference PQC-199	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/US 98/ 10070	International filing date (day/month/year) 15/05/1998	(Earliest) Priority Date (day/month/year)
Applicant NATIONAL SILICATES LTD.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 02 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing :



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2.



Certain claims were found unsearchable (See Box I).

3.



Unity of invention is lacking (see Box II).

4. With regard to the title,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the abstract,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D21C9/10 D21C9/16 D21C9/147

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 148 712 A (ATOCHEM) 17 July 1985 (1985-07-17) page 2, line 8 -page 3, line 17; example 1	1-3, 7-11, 15, 16, 19, 20, 24
A	WO 94 10374 A (SCA WIFSTA OESTRAND AB) 11 May 1994 (1994-05-11) page 3, line 32 -page 4, line 20	1, 4, 7-9, 12, 15-20, 24
A	US 4 915 785 A (SIMINOSKI GREGORY J ET AL) 10 April 1990 (1990-04-10) column 3, line 33 -column 4, line 56	1-25

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

24 May 2000

Date of mailing of the international search report

07/06/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bernardo Noriega, F

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0148712	A	17-07-1985	FR 2557605	A 05-07-1985
			AT 29537	T 15-09-1987
			AU 567787	B 03-12-1987
			AU 3724384	A 04-07-1985
			CA 1262805	A 14-11-1989
			DE 3466024	D 15-10-1987
			ES 539151	D 16-11-1985
			ES 8602173	A 01-03-1986
			FI 845121	A, B, 30-06-1985
			JP 1453574	C 10-08-1988
			JP 60181391	A 17-09-1985
			JP 62061716	B 23-12-1987
WO 9410374	A	11-05-1994	SE 500353	C 06-06-1994
			AU 5400294	A 24-05-1994
			SE 9203122	A 27-04-1994
US 4915785	A	10-04-1990	AU 623465	B 14-05-1992
			AU 4715989	A 28-06-1990
			CA 2005599	A 23-06-1990
			FR 2641010	A 29-06-1990
			GB 2227759	A, B 08-08-1990
			JP 3137287	A 11-06-1991
			NO 895234	A 25-06-1990
			NZ 231760	A 26-04-1991
			PT 92695	A, B 29-06-1990
			SE 8904313	A 24-06-1990
			ZA 8909502	A 26-09-1990

PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

LEWIS, Christopher, R.
Ratner & Prestia
Suite 301
One Westlakes, Berwyn
P.O. Box 980
Valley Forge, PA 19482-0980
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year)

24 November 2000 (24.11.00)

Applicant's or agent's file reference

PQC-199

International application No.

PCT/US98/10070

IMPORTANT NOTIFICATION

International filing date (day/month/year)

15 May 1998 (15.05.98)

1. The following indications appeared on record concerning:



the applicant



the inventor



the agent



the common representative

Name and Address

NATIONAL SILICATES LTD.
429 Kipling Avenue
Etobicoke, Ontario M8Z 5C7
Canada

State of Nationality

CA

State of Residence

CA

Telephone No.

Facsimile No.

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:



the person



the name



the address



the nationality



the residence

Name and Address

NATIONAL SILICATES PARTNERSHIP.
429 Kipling Avenue
Etobicoke, Ontario M8Z 5C7
Canada

State of Nationality

CA

State of Residence

CA

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary:

4. A copy of this notification has been sent to:



the receiving Office



the International Searching Authority



the International Preliminary Examining Authority



the designated Offices concerned



the elected Offices concerned



other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Sean Taylor

Telephone No.: (41-22) 338.83.38

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/10070

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D21C9/10 D21C9/16 D21C9/17

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 94 10374 A (SCA WIFSTA OESTRAND AB) 11 May 1994 (1994-05-11) page 3, line 32 -page 4, line 20	1, 4, 7-9, 12, 15-20, 24
A	US 4 915 785 A (SIMINOSKI GREGORY J ET AL) 10 April 1990 (1990-04-10) column 3, line 33 -column 4, line 56	1-25

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

24 May 2000

Date of mailing of the international search report

07/06/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 851 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bernardo Noriega, F

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.
PCT/US 98/10070

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0148712	A	17-07-1985	FR 2557605 A	05-07-1985
			AT 29537 T	15-09-1987
			AU 567787 B	03-12-1987
			AU 3724384 A	04-07-1985
			CA 1262805 A	14-11-1989
			DE 3466024 D	15-10-1987
			ES 539151 D	16-11-1985
			ES 8602173 A	01-03-1986
			FI 845121 A, B,	30-06-1985
			JP 1453574 C	10-08-1988
			JP 60181391 A	17-09-1985
			JP 62061716 B	23-12-1987
WO 9410374	A	11-05-1994	SE 500353 C	06-06-1994
			AU 5400294 A	24-05-1994
			SE 9203122 A	27-04-1994
US 4915785	A	10-04-1990	AU 623465 B	14-05-1992
			AU 4715989 A	28-06-1990
			CA 2005599 A	23-06-1990
			FR 2641010 A	29-06-1990
			GB 2227759 A, B	08-08-1990
			JP 3137287 A	11-06-1991
			NO 895234 A	25-06-1990
			NZ 231760 A	26-04-1991
			PT 92695 A, B	29-06-1990
			SE 8904313 A	24-06-1990
			ZA 8909502 A	26-09-1990

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference PQC-199	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US98/10070	International filing date (day/month/year) 15/05/1998	Priority date (day/month/year) 15/05/1998 NONE
International Patent Classification (IPC) or national classification and IPC D21C9/10		
Applicant NATIONAL SILICATES LTD		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 7 sheets, including this cover sheet.
 - ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

- This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 14/12/1999	Date of completion of this report 18.08.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Naeslund, P Telephone No. +49 89 2399 8614 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US98/10070

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-20 as originally filed

Claims, No.:

1-25 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	4-6,12-14,17,18,21-23,25
	No:	Claims	1-3,7-11,15,16,19,20,24
Inventive step (IS)	Yes:	Claims	None
	No:	Claims	1-25
Industrial applicability (IA)	Yes:	Claims	1-25
	No:	Claims	None

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US98/10070

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following document/s/:

- D1: EP-A-0 148 712 cited in the ISR
- D2: WO-A-94 10374 cited in the ISR
- D3: US-A-4 915 785 cited in the ISR
- D4: EP-B-0 677 124 (new citation)

1. Document **D1** (see page 2, line 8-page 3, line 17; example 1) discloses a combination of additives for use in a brightening stage of pulps containing less than 18 % lignin ("pate ecrue issue d'une cuisson Kraft de resineux"; i.e. a chemical pulp, compare also page 1, third paragraph of the present application) wherein said combination comprises an aqueous sodium silicate solution; an alkali agent added in an amount sufficient to maintain a pH of said solution at least about 8; and a magnesium compound which dissociates in said solution to form $Mg(OH)^+$ cations, wherein said magnesium compound is added in an amount to achieve, along with any other dissociated magnesium, an $Mg:SiO_2$ mass ratio of between about 1:46 to about 1:2 (calculated).

The subject-matter of claim 1 is therefore implicitly known from document **D1** (Article 33(2) PCT). The attention is also directed to document **D2** and **D3** both of which disclose the essential features of claim 1, that is a combination of additives for use in a brightening step of a cellulosic pulp including sodium silicate, an alkali agent, a pH of at least 8 and a magnesium compound which dissociates in the solution. To the skilled person it would have been obvious to apply the teachings in either of **D2** or **D3**, on the chemical pulps disclosed in document **D1**- all these processes are related to peroxide bleaching.

2. In view of **D1** none of claims 2,3,7-11,15,16,19,20 or 24 would appear novel either (Art. 33(2) PCT).

3. Claims 4 and 12 require that the magnesium compound is magnesium sulfate. Such a compound is however known from **D2**, page 4, line 10 and **D3** col. 4, line 10 (Art. 33(3) PCT).
4. The concentration ranges recited in claims 5,6,13 and 14 when not explicitly disclosed, are only a matter of routine optimization (Art. 33(3) PCT).
5. The lignin contents of less than 5% and 2% respectively, as recited in claims 17 and 18 when not inherently fulfilled by the chemical kraft pulps disclosed in document **D1** would be attained after initial commonly applied prebleaching stages (Art. 33(3) PCT).
6. The pressurization of alkaline peroxide bleaching steps belongs today to common practice. Normally this is done with air which is an oxygene-containing gas (Art. 33(3) PCT). Therefore claim 21 does not comprise any inventive matter.
7. Concerning independent claim 22, it differs in view of **D1** in substance by the pressurizing step. Pressurizing of peroxide bleaching steps however is as has already been set out common practise in the field (see e.g. **D4**, claim 1)(Art. 33(3) PCT).
8. The oxygen partial pressure as recited in claim 24 to be applied when not explicitly disclosed is a result of routine optimization (Art. 33(3) PCT).
9. No particular effect can be seen coupled to a molecular weight of at least 10.000 Daltons of the silicates as claimed in claim 25 can be seen (Art. 33(3) PCT). Moreover, this feature is merely one of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill, in order to solve the problem posed.
10. The industrial application would appear evident (Art. 33(4) PCT).

Re Item VII

Certain defects in the international application

1. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents **D1** to **D4** is not mentioned in the description, nor are these documents identified therein.
2. The two-part form should be applied to the independent claims.

Re Item VIII

Certain observations on the international application

1. Although claims 1,9,20,22 and 24 have been drafted as separate independent claims, they appear to relate effectively to the same subject-matter and to differ from each other only with regard to the definition of the subject-matter for which protection is sought and/or in respect of the terminology used for the features of that subject-matter. The aforementioned claims therefore lack conciseness. Moreover, lack of clarity of the claims as a whole arises, since the plurality of independent claims makes it difficult, if not impossible, to determine the matter for which protection is sought, and places an undue burden on others seeking to establish the extent of the protection.

Hence, claims 1,9,20,22 and 24 do not meet the requirements of Article 6 PCT.

In the present case it would appear appropriate with one independent claim in each category. In case the applicant maintains more than one independent claim in each category, it might upon entering the national/regional phase become necessary to raise an objection corresponding to Rule 13.1 PCT; i.e to assess whether a common inventive concept is present.

2. Nowhere in the application would there appear to be described how the lignin content has been measured let alone any correlation between any such measurements and the percentage of the lignin content in the pulps as appearing

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US98/10070

in e.g. claims 1, 9, 20, 22 and 24 (Article 6 PCT).

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

RATNER & PRESTIA
500 North Gulph Road
P.O. Box 980
VALLEY FORGE, PA 19482
ETATS-UNIS D'AMERIQUE

RECEIVED

AUG 23 2000

RATNER & PRESTIA

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year) 18.08.2000

Applicant's or agent's file reference
PQC-199

IMPORTANT NOTIFICATION

International application No.
PCT/US98/10070

International filing date (day/month/year)
15/05/1998

Priority date (day/month/year)
15/05/1998

Applicant
NATIONAL SILICATES LTD

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer

Fuerbass, C



Tel. +49 89 2399-8132



PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PQC-199	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US98/10070	International filing date (day/month/year) 15/05/1998	Priority date (day/month/year) 15/05/1998
International Patent Classification (IPC) or national classification and IPC D21C9/10		
Applicant NATIONAL SILICATES LTD		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 7 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input checked="" type="checkbox"/> Certain defects in the international application VIII <input checked="" type="checkbox"/> Certain observations on the international application 		
Date of submission of the demand 14/12/1999	Date of completion of this report 18.08.2000	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Naeslund, P Telephone No. +49 89 2399 8614 	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US98/10070

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-20 as originally filed

Claims, No.:

1-25 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	4-6,12-14,17,18,21-23,25
	No:	Claims	1-3,7-11,15,16,19,20,24
Inventive step (IS)	Yes:	Claims	None
	No:	Claims	1-25
Industrial applicability (IA)	Yes:	Claims	1-25
	No:	Claims	None

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US98/10070

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

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- D2: WO-A-94 10374 cited in the ISR
- D3: US-A-4 915 785 cited in the ISR
- D4: EP-B-0 677 124 (new citation)

1. Document **D1** (see page 2, line 8-page 3, line 17; example 1) discloses a combination of additives for use in a brightening stage of pulps containing less than 18 % lignin ("pate ecrue issue d'une cuisson Kraft de resineux"; i.e. a chemical pulp, compare also page 1, third paragraph of the present application) wherein said combination comprises an aqueous sodium silicate solution; an alkali agent added in an amount sufficient to maintain a pH of said solution at least about 8; and a magnesium compound which dissociates in said solution to form $Mg(OH)^+$ cations, wherein said magnesium compound is added in an amount to achieve, along with any other dissociated magnesium, an $Mg:SiO_2$ mass ratio of between about 1:46 to about 1:2 (calculated).

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2. In view of **D1** none of claims 2,3,7-11,15,16,19,20 or 24 would appear novel either (Art. 33(2) PCT).

3. Claims 4 and 12 require that the magnesium compound is magnesium sulfate. Such a compound is however known from **D2**, page 4, line 10 and **D3** col. 4, line 10 (Art. 33(3) PCT).
4. The concentration ranges recited in claims 5,6,13 and 14 when not explicitly disclosed, are only a matter of routine optimization (Art. 33(3) PCT).
5. The lignin contents of less than 5% and 2% respectively, as recited in claims 17 and 18 when not inherently fulfilled by the chemical kraft pulps disclosed in document **D1** would be attained after initial commonly applied prebleaching stages (Art. 33(3) PCT).
6. The pressurization of alkaline peroxide bleaching steps belongs today to common practice. Normally this is done with air which is an oxygene-containing gas (Art. 33(3) PCT). Therefore claim 21 does not comprise any inventive matter.
7. Concerning independent claim 22, it differs in view of **D1** in substance by the pressurizing step. Pressurizing of peroxide bleaching steps however is as has already been set out common practise in the field (see e.g. **D4**, claim 1)(Art. 33(3) PCT).
8. The oxygen partial pressure as recited in claim 24 to be applied when not explicitly disclosed is a result of routine optimization (Art. 33(3) PCT).
9. No particular effect can be seen coupled to a molecular weight of at least 10.000 Daltons of the silicates as claimed in claim 25 can be seen (Art. 33(3) PCT). Moreover, this feature is merely one of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill, in order to solve the problem posed.
10. The industrial application would appear evident (Art. 33(4) PCT).

Re Item VII

Certain defects in the international application

1. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents **D1** to **D4** is not mentioned in the description, nor are these documents identified therein.
2. The two-part form should be applied to the independent claims.

Re Item VIII

Certain observations on the international application

1. Although claims 1,9,20,22 and 24 have been drafted as separate independent claims, they appear to relate effectively to the same subject-matter and to differ from each other only with regard to the definition of the subject-matter for which protection is sought and/or in respect of the terminology used for the features of that subject-matter. The aforementioned claims therefore lack conciseness. Moreover, lack of clarity of the claims as a whole arises, since the plurality of independent claims makes it difficult, if not impossible, to determine the matter for which protection is sought, and places an undue burden on others seeking to establish the extent of the protection.

Hence, claims 1,9,20,22 and 24 do not meet the requirements of Article 6 PCT.

In the present case it would appear appropriate with one independent claim in each category. In case the applicant maintains more than one independent claim in each category, it might upon entering the national/regional phase become necessary to raise an objection corresponding to Rule 13.1 PCT; i.e to assess whether a common inventive concept is present.

2. Nowhere in the application would there appear to be described how the lignin content has been measured let alone any correlation between any such measurements and the percentage of the lignin content in the pulps as appearing

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US98/10070

in e.g. claims 1, 9, 20, 22 and 24 (Article 6 PCT).

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

RATNER & PRESTIA
500 North Gulph Road
P.O. Box 980
VALLEY FORGE, PA 19482
ETATS-UNIS D'AMERIQUE

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SEP 26 2000

attn: Mr. Chris

RATNER & PRESTIA

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NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

29.08.00

Applicant's or agent's file reference
PQC-199

IMPORTANT NOTIFICATION

International application No.
PCT/US98/10070

International filing date (day/month/year)
15/05/1998

Priority date (day/month/year)
15/05/1998

Applicant
NATIONAL SILICATES LTD

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

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Handwritten signature

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US98/10070

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US98/10070

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-20 as originally filed

Claims, No.:

1-24 with telefax of 16/08/2000

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☒ the claims, Nos.: 25
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	4-6,12-14,17,18,21-23
	No:	Claims	1-3,7-11,15,16,19,20,24
Inventive step (IS)	Yes:	Claims	None
	No:	Claims	1-24
Industrial applicability (IA)	Yes:	Claims	1-24
	No:	Claims	None

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following document/s/:

- D1: EP-A-0 148 712 cited in the ISR
- D2: WO-A-94 10374 cited in the ISR
- D3: US-A-4 915 785 cited in the ISR
- D4: EP-B-0 677 124 (new citation)

1. Document **D1** (see page 2, line 8-page 3, line 17; example 1) discloses a combination of additives for use in a brightening stage of pulps containing less than 18 % lignin ("pate ecrue issue d'une cuisson Kraft de resineux"; i.e. a chemical pulp, compare also page 1, third paragraph of the present application) wherein said combination comprises an aqueous sodium silicate solution; an alkali agent added in an amount sufficient to maintain a pH of said solution at least about 8; and a magnesium compound which dissociates in said solution to form $Mg(OH)^+$ cations, wherein said magnesium compound is added in an amount to achieve, along with any other dissociated magnesium, an $Mg:SiO_2$ mass ratio of between about 1:46 to about 1:2 (calculated). As to the feature "and wherein at least 25% of the silicates have a molecular weight of at least 10,000 Daltons", it is believed that this condition is equally present in the process according to **D1**, in view of the statements on page 9, third complete paragraph to page 10, second complete paragraph of the present application.

The subject-matter of claim 1 is therefore implicitly known from document **D1** (Article 33(2) PCT). The attention is also directed to document **D2** and **D3** both of which discloses the essential features of claim 1, that is a combination of additives for use in a brightening step of a cellulosic pulp including sodium silicate, an alkali agent, a pH of at least 8 and a magnesium compound which dissociates in the solution. To the skilled person it would have been obvious to apply the teachings in either of **D2** or **D3**, on the chemical pulps disclosed in document **D1**- all these

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US98/10070

processes are related to peroxide bleaching.

2. In view of **D1** none of claims 2,3,7-11,15,16,19,20 or 24 would appear novel either (Art. 33(2) PCT).
3. Claims 4 and 12 require that the magnesium compound is magnesium sulfate. Such a compound is however known from **D2**, page 4, line 10 and **D3** col. 4, line 10 (Art. 33(3) PCT).
4. The concentration ranges recited in claims 5,6,13 and 14 when not explicitly disclosed, are only a matter of routine optimization (Art. 33(3) PCT).
5. The lignin contents of less than 5% and 2% respectively, as recited in claims 17 and 18 when not inherently fulfilled by the chemical kraft pulps disclosed in document **D1** would be attained after initial commonly applied prebleaching stages (Art. 33(3) PCT).
6. The pressurization of alkaline peroxide bleaching steps belongs today to common practice. Normally this is done with air which is an oxygene-containing gas (Art. 33(3) PCT). Therefore claim 21 does not comprise any inventive matter.
7. Concerning independent claim 22, it differs in view of **D1** in substance by the pressurizing step. Pressurizing of peroxide bleaching steps however is as has already been set out common practise in the field (see e.g. **D4**, claim 1)(Art. 33(3) PCT).
8. The oxygen partial pressure to be applied as recited in claim 24, when not explicitly disclosed it would only be a result of routine optimization (Art. 33(3) PCT).
9. The industrial application would appear evident (Art. 33(4) PCT).

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US98/10070

Re Item VII

Certain defects in the international application

1. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents **D1** to **D4** is not mentioned in the description, nor are these documents identified therein.
2. The two-part form should be applied to the independent claims.
3. Metric units should be additionally stated; see eg inch, page 19, line 4.

Re Item VIII

Certain observations on the international application

1. Although claims 1,9,20,22 and 24 have been drafted as separate independent claims, they appear to relate effectively to the same subject-matter and to differ from each other only with regard to the definition of the subject-matter for which protection is sought and/or in respect of the terminology used for the features of that subject-matter. The aforementioned claims therefore lack conciseness. Moreover, lack of clarity of the claims as a whole arises, since the plurality of independent claims makes it difficult, if not impossible, to determine the matter for which protection is sought, and places an undue burden on others seeking to establish the extent of the protection.

Hence, claims 1,9,20,22 and 24 do not meet the requirements of Article 6 PCT.

In the present case it would appear appropriate with one independent claim in each category. In case the applicant maintains more than one independent claim in each category, it might upon entering the national/regional phase become necessary to raise an objection corresponding to Rule 13.1 PCT; i.e to assess whether a common inventive concept is present.

2. Nowhere in the application would there appear to be described how the lignin

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US98/10070

content has been measured let alone any correlation between any such measurements and the percentage of the lignin content in the pulps as appearing in e.g. claims 1, 9, 20, 22 and 24 (Article 6 PCT).

1 1. A combination of additives for use in a brightening stage of pulps
2 containing less than 18% lignin, said combination comprising: an aqueous solution of
3 sodium silicate; an alkali agent added in an amount sufficient to maintain a pH of said
4 solution at least about 8; and a magnesium compound which dissociates in said solution to
5 form $Mg(OH)^+$ cations, wherein said magnesium compound is added in an amount to
6 achieve, along with any other dissociated magnesium, an $Mg:SiO_2$ mass ratio of between
7 about 1:46 to about 1:2, and wherein at least 25% of the silicates have a molecular weight
8 of at least 10,000 Daltons.

3. A combination of additives in accordance with claim 1, wherein said alkali agent is added in an amount sufficient to maintain the pH of said solution within the range of from about 8 to about 12.

1 5. A combination of additives in accordance with claim 1, wherein:
2 said aqueous sodium silicate solution is added in an amount to achieve a
3 concentration of from about 0.14% to about 1.4% SiO₂ on pulp; and

1 6. A combination of additives in accordance with claim 5, wherein:
2 said aqueous sodium silicate solution is added in an amount to achieve a
3 concentration of from about 0.28% to about 1.12% SiO₂ on pulp; and

AMENDED SHEET

PQC-199

- 22 -

1 7. A combination of additives in accordance with claim 1, wherein
2 said alkali agent is selected from the group consisting of at least one of NaOH, Na₂O,
3 MgO, Mg(OH)₂, K₂O, KOH, CaO, and Ca(OH)₂.

1 8. A combination of additives in accordance with claim 1, wherein
2 said magnesium compound is selected from the group consisting of at least one of MgO,
3 MgCl₂, Mg(OH)₂ and MgNO₃.

1 9. An aqueous composition for use in a brightening stage of pulps
2 comprising:

3 pulp containing less than 18% lignin;

4 an aqueous solution of sodium silicate;

5 an alkali agent added in an amount sufficient to maintain the pH at least
6 about 8; and

7 a magnesium compound which dissociates in said solution to form
8 Mg(OH)⁺ cations, wherein said magnesium compound is added in an amount to achieve,
9 along with any other dissociated magnesium, an Mg:SiO₂ mass ratio of between about
10 1:46 to about 1:2, and wherein at least 25% of the silicates have a molecular weight of at
11 least 10,000 Daltons.

1 10. An aqueous composition in accordance with claim 9, wherein said
2 Mg:SiO₂ mass ratio is between about 1:15 to about 1:3.

1 11. An aqueous composition in accordance with claim 9, wherein said
2 alkali agent is added in an amount sufficient to maintain the pH of said solution within the
3 range of from about 8 to about 12.

1 12. An aqueous composition in accordance with claim 9, wherein said
2 magnesium compound is magnesium sulfate, added as MgSO₄ or MgSO₄·7H₂O.

1 13. An aqueous composition in accordance with claim 9, wherein:
2 said aqueous sodium silicate solution is added in an amount to achieve a
3 concentration of from about 0.14% to about 1.4% SiO₂ on pulp; and

PQC-199

- 23 -

4 said magnesium compound is added in an amount to achieve a
5 concentration of from about 0.01 % to about 0.2 % Mg on pulp.

1 14. An aqueous composition in accordance with claim 13, wherein:
2 said aqueous sodium silicate solution is added in an amount to achieve a
3 concentration of from about 0.28 % to about 1.12 % SiO₂ on pulp; and

4 said magnesium compound is added in an amount to achieve a
5 concentration of from about 0.02 % to about 0.2 % Mg on pulp.

1 15. An aqueous composition in accordance with claim 9, wherein said
2 alkali agent is selected from the group consisting of at least one of NaOH, Na₂O, MgO,
3 Mg(OH)₂, K₂O, KOH, CaO and Ca(OH)₂.

1 16. An aqueous composition in accordance with claim 9, wherein said
2 magnesium compound is selected from the group consisting of at least one of MgO,
3 MgCl₂, Mg(OH)₂ and MgNO₃.

1 17. An aqueous composition in accordance with claim 9, wherein said
2 pulp contains less than 5 % lignin.

1 18. An aqueous composition in accordance with claim 17, wherein said
2 pulp contains less than 2 % lignin.

1 19. An aqueous composition in accordance with claim 9 further
2 comprising hydrogen peroxide.

1 20. A method for brightening pulp comprising the steps of:
2 mixing pulp containing less than 18 % lignin with hydrogen peroxide, an
3 aqueous solution of sodium silicate; an alkali agent added in an amount sufficient to
4 maintain the pH of said solution at least about 8; and a magnesium compound which
5 dissociates in said solution to form Mg(OH)⁺ cations, wherein said magnesium compound
6 is added in an amount to achieve, along with any other dissociated magnesium, an
7 Mg:SiO₂ mass ratio of between about 1:46 to about 1:2, to form a mixture, and wherein
8 at least 25 % of the silicates have a molecular weight of at least 10,000 Daltons; and

PQC-199

- 24 -

9 heating said mixture to allow said mixture to react to cause a portion of
10 said lignin to degrade.

1 21. A method in accordance with claim 20 further comprising
2 pressurizing said mixture with an oxygen-containing gas.

1 22. A method for delignifying and brightening pulp comprising the
2 steps of:

3 mixing pulp containing less than 18% lignin with an aqueous solution of
4 sodium silicate; an alkali agent added in an amount sufficient to maintain the pH of said
5 solution at least about 8; and a magnesium compound which dissociates in said solution to
6 form $Mg(OH)^+$ cations, wherein said magnesium compound is added in an amount to
7 achieve, along with any other dissociated magnesium, an $Mg:SiO_2$ mass ratio of between
8 about 1:46 to about 1:2, to form a mixture, and wherein at least 25% of the silicates have
9 a molecular weight of at least 10,000 Daltons;

10 pressurizing said mixture with an oxygen-containing gas; and

11 heating said mixture to allow said mixture to react to cause a portion of
12 said lignin to degrade.

1 23. A method in accordance with claim 22 wherein the oxygen partial
2 pressure is in the range of between about 0.38 to about 1.48 MPa.

1 24. A method for brightening pulp containing transition metals and less
2 than 18% lignin, said method comprising the steps of:

3 forming a sodium silicate solution having a high percentage of high
4 molecular weight silicates by mixing sodium silicate and a magnesium compound which
5 dissociates in said solution to form $Mg(OH)^+$ cations; and

6 adding said sodium silicate mixture to said pulp to adsorb at least a portion
7 of said transition metals.

1 25. Canceled



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US98/10070 (22) International Filing Date: 15 May 1998 (15.05.98) (71) Applicants (for all designated States except US): NATIONAL SILICATES LTD. [CA/CA]; 429 Kipling Avenue, Etobicoke, Ontario M8Z 5C7 (CA). THE RESEARCH FOUNDATION OF STATE UNIVERSITY OF NEW YORK [US/US]; SUNY Plaza, Broadway and State Streets, Albany, NY 12246 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): EVANS, Timothy, D. [CA/CA]; 1295 Avon Crescent, Oakville, Ontario L6J 2T5 (CA). FRANCIS, Raymond, C. [CA/US]; 106 Craig Circle, Dewitt, NY 13214 (US). (74) Agents: LEWIS, Christopher, R. et al.; Ratner & Prestia, Suite 301, One Westlakes, Berwyn, P.O. Box 980, Valley Forge, PA 19482-0980 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: PEROXIDE, OXYGEN, AND PEROXIDE/OXYGEN BRIGHTENING OF CHEMICAL AND MIXED WASTE PULPS (57) Abstract <p>A composition and method for use in the peroxide, oxygen, or peroxide/oxygen stage of brightening pulps with less than 18 % lignin utilize a magnesium compound in a sodium silicate solution to form a higher percentage of high molecular weight silicates. Such high molecular weight silicates preferentially adsorb transition metal impurities which, if left in solution, would tend to decompose hydrogen peroxide and organic peroxides. Hydrogen peroxide is added to peroxide and peroxide/oxygen stages, while it is generated, along with organic peroxides, during an oxygen stage. Decomposition decreases the amount of peroxide that actually reacts with lignin and generates free radicals that attack the desired product, carbohydrate fibers. The high molecular weight silicates can be formed by using any magnesium compound which dissociates to form Mg(OH)⁺ cations, which in turn cause a silicate polymerization reaction. The formation of Mg(OH)⁺ cations from magnesium compounds occurs most readily over a pH range of at least about 8 and preferably between about 8 and about 12. The magnesium compound is added in an amount to achieve an Mg:SiO₂ mass ratio of between about 1:46 to about 1:2, and preferably between about 1:15 to about 1:3.</p>		

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- 1 -

PEROXIDE, OXYGEN, AND PEROXIDE/OXYGEN BRIGHTENING OF CHEMICAL AND MIXED WASTE PULPS

FIELD OF THE INVENTION

The present invention pertains to the brightening of chemical pulps and deinked, mixed office waste pulps, and particularly to the brightening of such pulps in a peroxide or peroxide/oxygen stage of brightening.

BACKGROUND OF THE INVENTION

The process of making paper from wood involves the following general stages: (1) bark removal; (2) wood chipping; (3) pulping; (4) brightening; and (5) forming a sheet of paper on a machine. During pulping, wood is reduced to its fibrous state, with a portion of the lignin content in the wood being removed. Pulps can be divided into two main categories - chemical and mechanical pulps - depending on how they are made from wood. Chemical pulping involves the use of chemical reagents to effect a separation of the cellulose fibers from the other wood components, such as lignin and other extraneous compounds. In the process, most of the hemicelluloses are also dissolved. Thus, the yield for chemical pulping is typically 40-50% on wood.

Mechanical pulping involves the reduction of wood to the fibrous state by mechanical means, such as by grinding logs into pulp by large revolving grindstones. These pulps are called "mechanical" because a significant amount of mechanical energy (grinding or refining) is required to break down the wood chips. Except for a few water soluble components, all of the constituents of the wood are present in the ground wood pulp. Thus, mechanical pulps are characterized by their high yield and high lignin content. For example, although chemical pulps contain only about 5% lignin (weight basis on pulp) after pulping, mechanical pulps typically contain greater than 20% lignin for hardwoods and 25% for softwoods after pulping.

In general, the brightening of chemical and mechanical pulps occur by different mechanisms. This difference in approach is due, in part, to the difference in lignin content between the chemical and mechanical pulps and to the

- 2 -

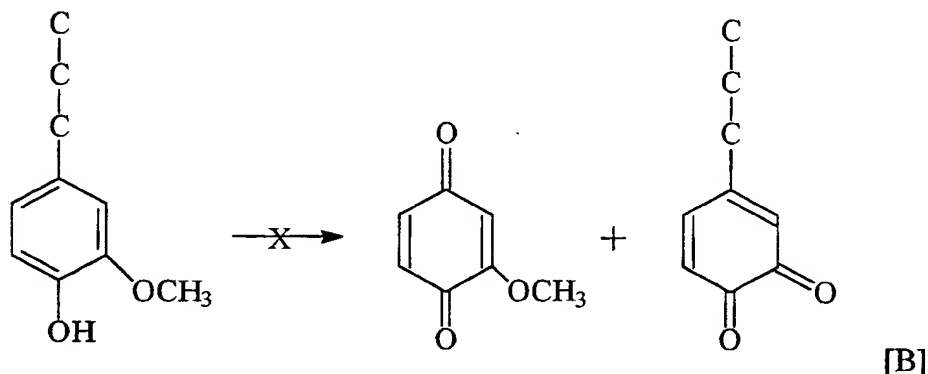
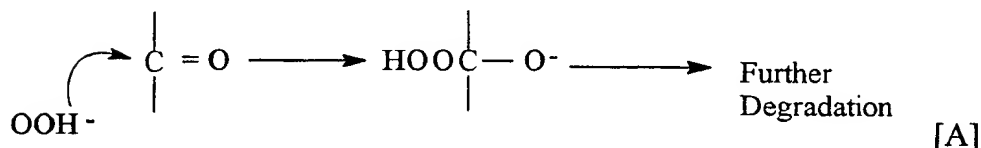
different nature of the lignin in chemical pulps than that in mechanical pulps. The remaining lignin in chemical pulps is typically more difficult to degrade than the majority of the lignin remaining in mechanical pulps. For example, chemical pulps, such as kraft pulps, are more difficult to brighten by H_2O_2 . Thus, instead of the 60°C bleaching temperature used for mechanical pulps, values in the range of 110°C are used for kraft pulps (which use sodium hydroxide and sodium sulfide as the primary chemical reagents). As another example of the differences in brightening the two different types of pulp, chlorine dioxide (ClO_2), a stable free radical, is involved in the brightening of more than 90 % of bleached kraft pulp produced in the U.S.A. per year. On the other hand, it has been reported that chlorine dioxide actually darkens mechanical pulps. In sum, results obtained with mechanical pulps cannot be considered as being predictive for chemical pulps.

Various additives have been proposed to improve the brightening process of mechanical pulps or mixed chemical/mechanical pulps having a high lignin content (i.e., above 20% by weight on pulp). Sodium silicate is widely used for hydrogen peroxide brightening of such pulps. It acts as a peroxide stabilizer and as a buffer during the bleaching reaction. Sodium silicate, in combination with a small dose of MgSO_4 , has long been known to improve the brightness of mechanical pulps. The two chemicals are known to form an intermediate that adsorbs or complexes transition metal species which would otherwise undesirably catalyze the decomposition of H_2O_2 . The two chemical combination is widely used in installations that bleach mechanical pulps. When magnesium sulfate has been used for such pulps, however, no increase in brightness has been observed when the $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ dose is increased above 0.05% on mechanical pulp (2.0 mmol/kg). Accordingly, previous researchers had no need to add more magnesium to their pulps.

Turning to the brightening of chemical pulps, some results have suggested that silicate has a negative effect on H_2O_2 bleaching of kraft pulps. In some cases, the inclusion of silicate lowered the brightness by 4.6 percentage points (measured as % GE brightness in accordance with TAPPI Standard T452 om-92) and by 2-7 percentage points.

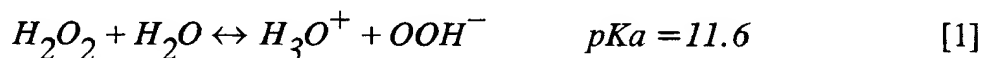
In peroxide brightening of mechanical pulps, the key is nucleophilic degradation of carbonyl compounds in the native lignin without the oxidation of phenols to o- and p- quinones, as shown below in reactions [A] and [B], respectively.

- 3 -



Reaction [A] is the desirable degradation of carbonyl compounds by the perhydroxyl anion, OOH^- . This reaction breaks down the carbonyl compounds, which absorb light in the visible range, to a more soluble form to be washed away by water. On the other hand, reaction [B] represents the undesirable formation of o- and p- quinones, which are less soluble in water and also absorb light in the visible range.

The perhydroxyl anion is generated by the dissociation of H_2O_2 as shown by equation [1] below. Mild conditions have to be used to prevent the oxidation of phenolics.



Mechanical pulps contain high concentrations of lignin and extractives whose negatively charged sites may complex transition metals. Also, some transition metal catalysis can be tolerated because lignin is a very good radical scavenger. It will scavenge the superoxide anion ($\cdot\text{O}_2^-$) and prevent wasteful decomposition to O_2 (equation [2]).



Actually, $\cdot\text{O}_2^-$ is nucleophilic and its reaction with lignin is reported to result in increased brightness. In sum, transition metal deactivation by magnesium silicates is important but not critical to the brightening of mechanical pulps.

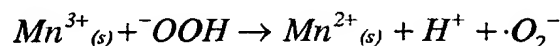
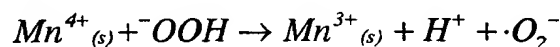
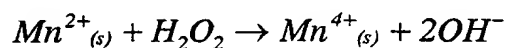
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Unlike softwood mechanical pulps which typically contain about 25% lignin (by weight on pulp), chemical pulps enter the final brightening stage with typically less than 2% lignin, which is typically colored and very difficult to oxidize. The approach with H_2O_2 is nucleophilic degradation by OOH^\cdot .

5 However, equation [2] becomes favorable because there is not a large amount of reactive lignin to scavenge $\cdot O_2^-$. Equation [2], in conjunction with equations [3] and [4], results in wasteful decomposition of H_2O_2 .

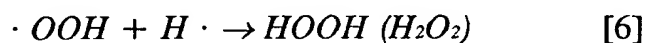


10 Equation [3] is favorable for Cu(I) and Fe(II) but not for Mn(II). A more probable mechanism for Mn(II) is outlined below. The subscripted s indicates soluble Mn(IV) and Mn(III).



15 Lignin degradation by OOH^\cdot requires a high temperature because of the unreactive nature of the lignin in chemical pulps. At 110°C, transition metal deactivation is extremely important.

With respect to O_2 delignification, a simple and well-accepted scheme for free radical generation is provided below. RH is a reactive structure in the solution phase.



(Abstraction of H atom from lignin)



25 H_2O_2 and ROOH will be affected by transition metals in the same manner as in a peroxide/oxygen stage. Thus, the oxygen stage is similar to the peroxide/oxygen stage in that they both involve heterolytic (i.e., ionic) reactions and homolytic (i.e., free radical) reactions. In addition, they are both similar in that both rely on

- 5 -

hydrogen peroxide, either as added in the peroxide/oxygen stage or as generated in reaction [6] above in the oxygen stage, to perform a brightening function. It is assumed that organic peroxides (ROOH in equation [8]) generated during oxygen delignification dissociate to form ROO⁻ nucleophiles that brighten lignin.

5 Accordingly, in both stages (as well as in a peroxide stage), one must be concerned about transition metals undesirably catalyzing free radical reactions.

SUMMARY OF THE INVENTION

The present invention provides a combination of additives and methods for brightening pulps containing less than 18% lignin. The invention can
10 be used in either the peroxide, oxygen, or peroxide/oxygen brightening stages. The additives according to the present invention include an aqueous sodium silicate solution, an alkali agent, and a magnesium compound which dissociates in the solution to form Mg(OH)⁺ cations. The alkali agent is added in an amount sufficient to maintain a pH of at least about 8, and the magnesium compound is
15 added in an amount to achieve, along with any other dissociated magnesium, an Mg:SiO₂ mass ratio of between about 1:46 to about 1:2.

A method for brightening pulp according to the present invention involves mixing pulp containing less than 18% lignin with an aqueous sodium silicate solution, an alkali agent, and a magnesium compound which dissociates in
20 the solution to form Mg(OH)⁺ cations. The alkali agent and magnesium compound are added to achieve the same pH range and weight ratio mentioned above. The method also includes heating the mixture to allow the mixture to react to cause a portion of the lignin in the pulp to degrade.

According to another embodiment of the present invention directed
25 to the peroxide or peroxide/oxygen brightening stages, a method for brightening pulp containing transition metals, hydrogen peroxide, and less than 18% lignin includes first forming a sodium silicate mixture having a high percentage of high molecular weight silicates. This is accomplished by mixing sodium silicate and a magnesium compound which dissociates in the solution to form Mg(OH)⁺ cations.
30 This sodium silicate mixture is then added to the pulp to adsorb at least a portion of the transition metals.

The present invention also includes an aqueous composition for use in brightening pulps. The composition includes pulp containing less than 18% lignin, an aqueous sodium silicate solution, an alkali agent, and a magnesium
35 compound which dissociates in the solution to form Mg(OH)⁺ cations. The alkali

- 6 -

agent and magnesium compound are added to achieve the same pH range and weight ratio mentioned above.

It is to be understood that both the foregoing general description and the following detailed description are exemplary, but are not restrictive, of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to the brightening of certain pulps during peroxide, oxygen, or peroxide/oxygen brightening. As used herein, the term "brightening stage" shall mean either a peroxide stage, an oxygen stage, or a peroxide/oxygen stage. The typical operating conditions and conventional additives to these stages are well known. During such brightening, hydrogen peroxide serves to degrade carbonyl groups of lignin, rendering them more water soluble. In the absence of such degradation, lignin would remain in the pulp, causing the brightness of the pulp to remain lower than would be if such lignin were removed. Transition metals present in the pulp undesirably react with hydrogen peroxide thereby precluding hydrogen peroxide from serving its function of degrading lignin. The present invention is based in part on the recognition that higher molecular weight silicates assist in adsorbing transition metals thus preventing them from undesirably reacting with hydrogen peroxide. The present invention is also based on the recognition that $\text{Mg}(\text{OH})^+$ plays a significant role in the molecular weight distribution of a sodium silicate solution. More particularly, the presence of $\text{Mg}(\text{OH})^+$ in a sodium silicate solution, over a certain $\text{Mg}:\text{SiO}_2$ mass ratio, enhances the formation of higher molecular weight silicates.

Accordingly, the present invention is directed to various compositions and methods embodying this concept. The invention provides a combination of additives (either to hydrogen peroxide, oxygen, or a combination thereof, depending on which one of the three brightening stages is being employed) for brightening pulps containing less than 18% lignin. In this case, these additives include an aqueous sodium silicate solution, an alkali agent, and a magnesium compound which dissociates in the solution to form $\text{Mg}(\text{OH})^+$ cations. The invention also encompasses an aqueous composition for use in brightening pulps comprising pulp containing less than 18% lignin, hydrogen peroxide (either as an additive or as reacted from reaction [6] above), an aqueous sodium silicate solution, an alkali agent, and a magnesium compound which dissociates in the

- 7 -

solution to form $\text{Mg}(\text{OH})^+$ cations. The present invention also provides a method for brightening pulp including forming a mixture of the pulp, hydrogen peroxide, aqueous sodium silicate solution, alkali agent, and magnesium compound, then heating the mixture to allow it to react to cause a portion of the lignin to degrade. Finally, the invention is characterized as a method for brightening pulp containing transition metals and less than 18% lignin. This method includes the steps of forming a sodium silicate mixture having a high percentage of high molecular weight silicates by mixing sodium silicate and a suitable magnesium compound, and adding the sodium silicate mixture to the pulp.

The pulp used in connection with the present invention is defined broadly as any pulp having less than 18% lignin (on pulp). Unless otherwise specified, all percentages of lignin include all forms of lignin and are given as weight percentages of the total pulp, on a dry weight basis, so that 18% lignin means that there are 18 grams of lignin in a 100 gram sample of pulp (excluding the weight of water).

Stated another way, the invention can be used with any pulp in which more than 50% of the lignin (by weight, on wood) is removed during pulping. This means that more than half of the original lignin present in the wood is removed during the pulping process. For softwoods, having an average lignin content of 28.6% (by weight, on wood), the removal of half of the original lignin content of the wood during a conventional chemical pulping process results in a pulp having 23.3% lignin (on pulp). For hardwoods, having an average lignin content of 24.1% (by weight, on wood), the removal of half of the original lignin content of the wood during a conventional chemical pulping process results in a pulp having 18.0% lignin (on pulp). The development of these final lignin contents factors in the yield from conventional chemical pulping processes. Thus, any pulp with less than 18% lignin (on pulp) would typically include at least some pulp which was processed by chemical pulping or was derived from a wood having a relatively low initial content of lignin.

In general, chemical pulping processes are continued until the lignin content is reduced to about 5% (on pulp) or less. It is preferable to use the present invention to brighten such pulps. In addition, chemical pulps typically undergo further delignification before the final brightening stage (i.e., peroxide or peroxide/oxygen) such that the pulps contain about 1-2% lignin before the final brightening stage. Pulps brightened by the present invention can also include such pulps which have been further delignified. The present invention can also be used

- 8 -

to brighten pulps having recycled pulps, in which chemical and mechanical pulps are mixed, as long as the average lignin content is less than about 18%. Pulps brightened by the present invention also include semichemical pulps with lignin content varying from approximately 10 to 18%. In Example 4 below, bleached and unbleached samples of de-inked mixed office waste consisting of 65% sorted white ledger and 35% office pack were obtained from a mill in the American Midwest.

The additives of the present invention are used in the peroxide, oxygen, or peroxide/oxygen stages of brightening. The process parameters of these stages are well known. For example, a typical charge of peroxide loading is 20 kg of hydrogen peroxide per metric ton of pulp. The hydrogen peroxide is mixed while the mixture is heated, typically to a temperature of between about 90°C to about 130°C, often 110°C. Water is also added, typically to achieve a consistency of about 15% solids. Of course, reaction time, temperature, and consistency are all interrelated and can be varied in a known manner. A hydrogen peroxide/oxygen stage is similar to a hydrogen peroxide stage except that the slurry is pressurized with oxygen.

An oxygen stage is similar to a hydrogen peroxide/oxygen stage except that no hydrogen peroxide is added. Oxygen delignification is also conducted over a wider consistency range (10% to 35% solids) but 12% to 15% solids is typical. In general, an oxygen stage does not brighten as well as a peroxide stage or as a peroxide/oxygen stage. Oxygen or an oxygen-containing gas (such as air) can be used to pressurize the mixture, and the partial pressure of oxygen typically ranges between 0.38 MPa and 1.48 MPa.

An additive of the present invention is an aqueous sodium silicate solution. Any commercially available aqueous sodium silicate solution may be used, although it is preferable to use as pure of a sodium silicate solution as is practically possible. The sodium silicate solution may be added in an amount to achieve a concentration of from about 0.14% to about 1.4% SiO₂ on pulp. Preferably, the sodium silicate solution is added in an amount to achieve a concentration of from about 0.28% to about 1.12% SiO₂ on pulp.

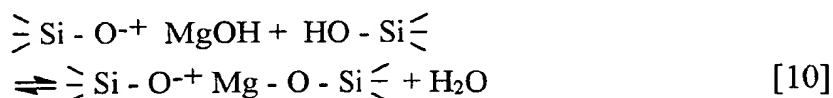
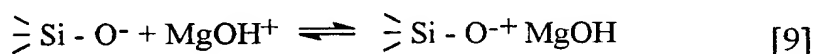
Another additive according to the present invention is a magnesium compound which dissociates in the solution to form Mg(OH)⁺ cations. The magnesium compound should be added in an amount to achieve, along with any other dissociated magnesium, an Mg:SiO₂ mass ratio of between about 1:46 to

- 9 -

about 1:2. Preferably, the Mg:SiO₂ mass ratio is between about 1:15 to about 1:3. Most preferably, the Mg:SiO₂ mass ratio is between about 1:10 to about 1:3. The mass ratio is of the total magnesium available for formation into Mg(OH)⁺, including any of the magnesium added and any magnesium inherent in the pulp and existing in a form which readily dissociates and forms Mg(OH)⁺ over a pH range of at least 8:

The magnesium compound is added in an amount to achieve an actual concentration of from about 0.01% to about 0.2% Mg on pulp (again including any other source of available magnesium). More preferably, the magnesium compound is added in an amount to achieve a concentration of from about 0.02% to about 0.2% Mg on pulp. Preferably, the magnesium compound is magnesium sulfate, added as MgSO₄ or MgSO₄·7H₂O. Alternatively, the magnesium compound is MgO, MgCl₂, Mg(OH)₂ and/or MgNO₃, among others. Any number of magnesium compounds can be used, as long as they readily form Mg(OH)⁺ at pH values of at least 8 and are not detrimental to process equipment.

A critical step in the present invention is the formation of the hydrolyzed magnesium cation Mg(OH)⁺. It is believed that this cation neutralizes dissociated silanol groups and causes silicate polymerization, as summarized by the equations written below:



Another additive of the present invention is an alkali agent added in an amount sufficient to maintain a pH of the solution of at least about 8. At pH values of at least about 8, magnesium exists as Mg(OH)⁺ in an amount sufficient to initiate reaction [9] above. More preferably, the alkali agent is selected and added in an amount sufficient to maintain the pH to a range of between 8 and 12. The alkali agent may be NaOH, Na₂O, MgO, Mg(OH)₂, K₂O, KOH, CaO, and/or Ca(OH)₂. Preferably, the non-calcium containing compounds are selected to minimize the formation of silicate scales. Such silicate scales can be detrimental to the quality of the paper product and must be removed periodically resulting in costly stoppages of the process. Because MgO and Mg(OH)₂ can serve two functions, namely that as the magnesium compound which readily forms

- 10 -

$\text{Mg}(\text{OH})^+$ and as an alkali agent, then the magnesium compound and alkali agent can be combined as one additive in some cases.

According to a method of the present invention, the pulp is brightened by mixing the pulp with hydrogen peroxide, an aqueous sodium silicate solution, an alkali agent added in an amount sufficient to maintain the pH of the solution at least about 8, and a magnesium compound which dissociates in the solution to form $\text{Mg}(\text{OH})^+$ cations, wherein the magnesium compound is added in an amount to achieve, along with any other dissociated magnesium, an $\text{Mg}:\text{SiO}_2$ mass ratio of between about 1:15 to about 1:3. This mixture is then heated, which allows the mixture to react to cause a portion of the lignin to degrade (i.e., to break down into a more soluble form to be washed away). In the case where a hydrogen peroxide/oxygen stage is used, the mixture is also pressurized with oxygen, in a known manner. While continuously heated, the chemicals are mixed into the pulp slurry which is retained at an elevated temperature for a period of time sufficient to allow the degradation reactions of the lignin to occur. This typically is between 30 minutes and four hours, depending on the temperature and concentration of the additives in the pulp. Typically, the mixture is heated to a temperature of between about 90°C and about 130°C.

As mentioned above, the present invention relies on the formation of high molecular weight silicates to adsorb transition metals to avoid the decomposition of hydrogen peroxide by transition metals. Accordingly, the present invention can be characterized as a method for brightening pulp by forming a sodium silicate solution having a high percentage of high molecular weight silicates by mixing sodium silicate and a magnesium compound which dissociates in the solution to form $\text{Mg}(\text{OH})^+$ cations. Then, the sodium silicate solution is added to the pulp to adsorb at least a portion of the transition metals of the pulp. Any increased amount of higher molecular weight silicates appears to improve the adsorption of transition metals, but it is preferable that the constituents are added such that the sodium silicate solution has at least 25% of the silicates with a molecular weight of at least 10,000 daltons.

It is not believed that the order of addition is important to the functioning of the present invention. Typically, the magnesium compound is Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and is either first dissolved in water or dissolved directly in a commercial aqueous sodium silicate solution. Then the alkali agent(s) is added followed by H_2O_2 . The combination is then mixed into the pulp slurry.

- 11 -

EXAMPLES

The following examples are included to more clearly demonstrate the overall nature of the invention. These examples are exemplary, not restrictive, of the invention.

Example 1

A kraft pulp was delignified by the ODEop partial sequence and had a kappa number of 2.7 and a viscosity of 19.0 cp. The ODEop partial sequence is called elemental chlorine-free or ECF. The pulp had a low initial Mg content (<50 ppm). The pulp was P/O ($P=H_2O_2$; $O=O_2$) bleached at 12% consistency and 110°C for 2 hours using reagent grade H_2O_2 , NaOH and $MgSO_4 \cdot 7H_2O$. A technical grade sodium silicate solution sold by Fisher Scientific, which contained some transition metals, was used. An H_2O_2 charge of 1.5% by weight on pulp was used with 2.0-2.3% NaOH by weight on pulp. The initial O_2 pressure for all P/O experiments was 0.38 MPa.

A first series of experiments was run to determine the effect of magnesium sulfate addition on the brightening of this ECF pulp. Table 1 shows both percentage of the constituents in each sample added to the pulp (on a dry weight basis) and the brightness, yield, viscosity, and residual H_2O_2 . Samples 1 through 4 have the same amount of silicate, sodium hydroxide, and hydrogen peroxide, while the amount of the magnesium compound (in this case, magnesium sulfate) increases from Samples 1 through 4. In all of the tables in the examples, "silicate" refers to the weight percent of a 41 Bé silicate solution (28.7% SiO_2) that was added. For all examples, the brightness was determined in accordance with TAPPI Standard T452 om-92. In addition, the pulp yield is the mass of washed pulp from the P or P/O stage divided by the mass of the feed to the stage. The viscosity and residual hydrogen peroxide (given as a percentage of the initial dose) were determined by known methods, including TAPPI Standard T230 om-94 for viscosity and iodometric titration for residual H_2O_2 .

- 12 -

Table 1

Effect of Magnesium Sulfate Application on P/O Bleaching of
First ECF Kraft Pulp

	Sample 1	Sample 2	Sample 3	Sample 4
Silicate, % on pulp	4.0	4.0	4.0	4.0
NaOH, % on pulp	2.3	2.3	2.3	2.3
H ₂ O ₂ , % on pulp	1.5	1.5	1.5	1.5
MgSO ₄ ·7H ₂ O % on pulp	0.0	0.25	0.5	0.75
SiO ₂ , % on pulp	1.148	1.148	1.148	1.148
Mg, % on pulp	0.0	0.025	0.050	0.075
Mg:SiO ₂ mass ratio	0	1:46	1:23	1:15
End pH	10.2	10.5	11.0	11.2
Brightness, %	79.8	84.0	84.2	85.3
Yield, %	97.2	97.7	98.1	98.2
Viscosity, cp	8.8	11.4	13.5	14.1
Residual H ₂ O ₂ , %				
30 Minutes	2	25	35	33
60 Minutes	0	15	22	30
120 Minutes	0	2	7	10

Table 1 shows that an MgSO₄·7H₂O charge of 0.25% on pulp (250 ppm Mg on pulp) increased brightness significantly, namely from 79.8% to 84.0%. Also, the brightness increased further when 0.50 and 0.75% MgSO₄·7H₂O was used. The interesting and totally novel result from Table 1 is the increase in pulp yield caused by the addition of magnesium sulfate. Kraft pulps can be dissolved in a solution of cupriethylenediamine, and the viscosity of the solution is an indicator of the degree of polymerization of the cellulose in the pulp. It can be seen that a higher charge of magnesium sulfate also resulted in higher viscosities (less depolymerization of cellulose during H₂O₂ brightening). However, the lowest viscosity (no MgSO₄·7H₂O) corresponds to an average DP of 815. It is unlikely that cellulose molecules of such high DP would solubilize. Therefore, it appears that hemicelluloses were being dissolved. Most likely, the free radicals from H₂O₂ decomposition were causing depolymerization of the hemicelluloses to a degree that resulted in their solubilization.

- 13 -

Example 2

A second ECF pulp sample was obtained from the same mill serving as the source of the pulp used in Example 1. It had a kappa number of 2.4 and a viscosity of 20.5 cp. The transition metal content of the first ECF pulp was not measured but the second pulp contained 6 ppm Mn, 8 ppm Fe, and 2 ppm Cu. These values were lowered to 0.3, 3.7 and 1.5 ppm, respectively, after treatment with NaDTPA. Sample 2 was bleached at 100°C, while Samples 1, 3, and 4 were bleached at 110°. Table 2 varies the charge of sodium silicate, with Samples 1 and 2 having no silicate added, while Samples 3 and 4 have a 2.0 and 4.0 % charge, respectively.

Table 2
Effect of Silicate on P/O Bleaching of Second ECF Kraft Pulp.
Chelated Pulp: 0.3 ppm Mn, 3.7 ppm Fe and 1.5 ppm Cu

	Sample 1	Sample 2	Sample 3	Sample 4
Silicate, % on pulp	0.0	0.0	2.0	4.0
NaOH, % on pulp	2.0	2.0	2.0	2.0
H ₂ O ₂ , % on pulp	1.5	1.5	1.5	1.5
MgSO ₄ · 7H ₂ O % on pulp	0.5	0.5	1.0	0.5
SiO ₂ , % on pulp	0.0	0.0	0.574	1.148
Mg, % on pulp	0.05	0.05	0.10	0.05
Mg:SiO ₂ mass ratio	NA*	NA*	1:6	1:23
End pH	10.9	10.9	10.5	10.9
Brightness, %	85.1	84.3	85.7	85.3
Yield, %	98.0	98.3	98.2	98.6
Viscosity, cp	12.6	13.7	16.3	13.7
Residual H ₂ O ₂ , %				
30 Minutes	24.9	31.5	38.2	41.5
60 Minutes	10.0	19.9	28.2	31.5
120 Minutes	3.3	6.6	14.9	14.9

*Not applicable

Table 2 shows slight increases in brightness and yield of the chelated sample when the amount of sodium silicate is increased. The low transition metal contents of this pulp, particularly the 0.3 ppm Mn, can be achieved in only a few commercial installations. More significantly, the presence of sodium silicate

- 14 -

shows a significant increase in residual hydrogen peroxide, which is important in maintaining brightness. In the absence of silicate, the H_2O_2 residual for most pulp samples would be zero after two hours at 110°C .

Example 3

Four more samples of the same ECF pulp used in Example 2, having a kappa number of 2.4 and a viscosity of 20.5 cp, were tested. In this case, the pulp was unchelated. In Samples 1 and 2 below, the temperature of the stage was 90°C while the temperature of Samples 3 and 4 was 110°C . Samples 1 and 3 contained no silicate, while Samples 2 and 4 did.

Table 3

Effect of Temperature on P/O Bleaching of Second ECF Kraft Pulp.
Unchelated Pulp: 6 ppm Mn, 8 ppm Fe and 2 ppm Cu

	Sample 1	Sample 2	Sample 3	Sample 4
Temperature, $^\circ\text{C}$	90	90	110	110
Silicate, % on pulp	0	2.0	0	2.0
NaOH, % on pulp	2.0	2.0	2.0	2.0
H_2O_2 , % on pulp	1.5	1.5	1.5	1.5
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ % on pulp	0.5	1.0	0.5	1.0
SiO_2 , % on pulp	0.0	0.574	0.0	0.574
Mg, % on pulp	0.05	0.1	0.05	0.1
Mg: SiO_2 mass ratio	NA	1:6	NA	1:6
End pH	11.3	11.6	9.9	10.9
Brightness, %	78.0	79.9	79.7	81.8
Yield, %	98.5	98.7	97.9	98.5
Viscosity, cp	15.4	15.7	11.5	14.1
Residual H_2O_2 , %				
30 Minutes	3.3	18.2	1.7	10.0
60 Minutes	1.7	10.0	0.0	5.0
120 Minutes	0.0	5.0	0.0	3.3

Table 3 shows that, at either temperature, the inclusion of sodium silicate improves the brightening process. At 90°C , a sample having sodium silicate gave no noticeable improvement in yield but 1.9% increase in brightness. At 110°C , a sample including sodium silicate caused a 0.6% increase in yield and a 2.1% increase in brightness. Also, as before, the presence of sodium silicate

- 15 -

showed a significant increase in residual hydrogen peroxide, which is important in maintaining brightness.

Example 4

Bleached and unbleached samples of de-inked, mixed office waste (MOW) consisting of 65% sorted white ledger and 35% office pack were obtained from a mill in the American Midwest. This pulp sample was from almost exclusively chemical pulps. The properties of the samples are summarized in Table 4. High positive b* value indicates a yellowish tint and a high negative value indicates a bluish tint. A high positive a* value indicates a reddish tint and a high negative value indicates a greenish tint. The aim of bleaching is to decrease the absolute a* and b* values to as close to zero and increase the L* value as high as possible. As shown in Table 4, the effect of the addition of silicate and magnesium sulfate to MOW was determined.

Table 4
Effect of Silicate Addition on P/O Bleaching of Mixed Office Waste (MOW)

Pulp ¹	MOW	MOW	BL. MOW	BL. MOW
Silicate, % on pulp	0.0	4.0	0.0	4.0
NaOH, % on pulp	2.3	2.3	2.3	2.3
H ₂ O ₂ , % on pulp	1.5	1.5	1.5	1.5
MgSO ₄ ·7H ₂ O on pulp	0.5	0.5	0.5	0.5
SiO ₂ , % on pulp	0.0	1.148	0.0	1.148
Mg, % on pulp	0.05	0.05	0.05	0.05
Mg:SiO ₂ mass ratio	NA	1:23	NA	1:23
End pH	10.1	10.2	10.0	10.0
Brightness, %	77.9	80.4	85.4	88.3
L*	91.51	91.86	94.79	95.24
a*	-0.46	0.22	0.27	-0.07
b*	1.67	0.73	1.68	0.48
Yield, %	95.4	96.5	97.3	97.4
Viscosity, cp	9.8	11.0	9.7	11.1
Residual H ₂ O ₂ , % of Applied				
30 Minutes	2	27	3	28
60 Minutes	0	10	1	15
120 Minutes	0	5	0	7

- 16 -

¹Mixed office waste (MOW) pretreated with 0.2% DTPA: Brightness, 74.2; $L^*=89.78$; $a^*=0.76$; $b^*=1.77$. Commercially bleached mixed office waste (BLMOW) pretreated with 0.2% DTPA: Brightness, 83.6, $L^*=94.4$; $a^*=0.28$; $b^*=1.72$.

It can be seen (footnotes of Table 4) that H_2O_2 bleaching in the mill ($\sim 1.0\%$ H_2O_2 , $\sim 95^\circ C$) did not significantly lower the b^* value. Both the unbleached and commercially bleached samples were treated with Na_5DTPA then brightened with 1.5% H_2O_2 at $110^\circ C$. For the unbleached sample, the inclusion of 4.0% silicate resulted in an improvement of 2.5 brightness points. The a^* and b^* values were closer to zero as well. Similar benefits were obtained when the commercially bleached pulp was brightened further. Without silicate, no significant decrease in b^* was obtained. A high temperature and high H_2O_2 residuals apparently are required to destroy the colored contaminants responsible for the b^* value. The inclusion of silicate increased the yield of the unbleached pulp by 1.1% .

Example 5

The results in Table 1 showed increased brightness with an increase in the dose ratio of $MgSO_4 \cdot 7H_2O$:sodium silicate (41 Bé). The dose ratio was increased further in Table 2 where 2% sodium silicate and 1.0% $MgSO_4 \cdot 7H_2O$ on pulp were used (i.e., Sample 3 of Table 2), which resulted in the highest brightness (85.7%) for the ECF pulps. In this Example, the effect of dose ratio on the brightening of a totally chlorine-free (TCF) pulp is investigated.

The TCF pulp (kraft) was from a Swedish mill and it had a kappa number of 7.4 and a viscosity of 23.4 cp. It also contained 1.9 ppm Mn, 4.7 ppm Fe, and 0.8 ppm Cu. After it was acid-washed it contained 0.1 ppm Mn, 4.0 ppm Fe, and 0.8 ppm Cu. The acid-washed pulp was brightened with various dose ratios of $MgSO_4 \cdot 7H_2O$:sodium silicate. The H_2O_2 and NaOH charges were 2.0% and 2.5% on pulp, respectively, and the pulps were brightened for two hours at $110^\circ C$ and 12% consistency.

Table 5
Effect of Silicate and $MgSO_4 \cdot 7H_2O$ on
P/O Bleaching of Acid-Washed TCF Pulps

	Sample 1	Sample 2	Sample 3	Sample 4
Silicate, % on pulp	0	4.0	2.0	1.0
NaOH, % on pulp	2.5	2.5	2.5	2.5
H_2O_2 , % on pulp	2.0	2.0	2.0	2.0

- 17 -

	Sample 1	Sample 2	Sample 3	Sample 4
MgSO ₄ ·7H ₂ O % on pulp	0.5	0.5	1.0	1.0
SiO ₂ , % on pulp	0	1.148	0.574	0.287
Mg, % on pulp	0.05	0.05	0.10	0.10
Mg:SiO ₂ mass ratio	NA	1:23	1:6	1:3
End pH	10.5	11.3	10.9	10.8
Brightness, %	75.4	78.2	79.4	77.9
Yield, %	96.3	98.2	98.3	98.0
Viscosity, cp	9.1	13.1	15.5	12.8
Residual H ₂ O ₂ , %				
30 Minutes	15	32	37	31
60 Minutes	4	19	16	8
120 Minutes	0	5	5	1

The brightness and yield were relatively low when silicate was excluded (Sample 1 of Table 5). The highest brightness was obtained with MgSO₄·7H₂O:sodium silicate dose ratio of 1%:2%. The next highest brightness was for dose ratio 0.5%:4%, followed by 1%:1%.

5 A general trend from the first five tables is that, for a given temperature, higher brightness and yields are obtained as H₂O₂ stabilization is improved (higher residuals). There is not an exact correlation because, for these experiments, the accuracy on H₂O₂ residual was about $\pm 5\%$ of the initial charge. However, final brightness in Table 5 correlates with H₂O₂ residual after 30
10 minutes.

The three dose ratios in Table 5, i.e. 0.5:4.0; 1.0:2.0; and 1.0:1.0, were used in a pulp-free system to deactivate 1 ppm, each Mn²⁺, Fe³⁺, and Cu²⁺ added simultaneously to the alkaline solution. For each dose ratio, the initial solution phase concentrations of H₂O₂, MgSO₄·7H₂O, and sodium silicate were
15 identical to when pulp was present. In the absence of pulp, less NaOH was required to achieve pH 11.2 taken as a rough average for P/O bleaching. The solutions were retained at 110°C for two hours then cooled and ultra-filtration was used to separate high and low molecular weight silicates. Membranes with 10,000 MW cutoff were used.

- 18 -

The results will be analyzed in terms of ppm Si in solution. The 41 Bé silicate solution that was used contained 28.7% SiO₂. Therefore 4% silicate on pulp corresponds to 1.148 SiO₂ on pulp or 0.536% Si on pulp. One hundred grams of pulp at 12% consistency is associated with 733 mL of solution (assuming a specific gravity of 1.0). Therefore, the Si concentration is 0.536 g in 733 mL or 0.731 g/L (~730 ppm). The solutions passing through the membrane were analyzed for Si, Mn, Fe and Cu concentrations by ICP spectroscopy. The results are presented in Table 6.

Table 6

Mg and Silicate Conc., ppm in Solution	Conc. Passing Through Membrane			
	Si	Mn	Fe	Cu
68 ppm Mg* + 730 ppm Si	617	0.008	0.023	0.027
136 ppm Mg + 365 ppm Si	194	0.001	0.001	0.016
136 ppm Mg + 183 ppm Si	56	0.004	0.001	0.018

*0.5% MgSO₄ · 7H₂O on pulp

Table 6 shows that in the case of 0.5% MgSO₄·7H₂O and 4% silicate, 85% of the Si passes through the membrane as low molecular weight compounds. However, less than 3% of the Fe and Cu and less than 1% of the Mn pass through. The transition metals appear to be bound to the high molecular weight silicate retained on the membrane. The data would suggest that 1.0% MgSO₄·7H₂O and 2.0% silicate give the best transition metal deactivation, particularly of Mn which is believed to be the most aggressive catalyst for H₂O₂ decomposition. The significance of the differences between 1, 4, and 8 ppb Mn or 16, 18 and 27 ppb Cu in solution might be deemed insignificant. However, there is no doubt that it is the high molecular weight silicate that adsorbs or complexes the transition metals. The amount of high molecular weight silicate (greater than 10,000 daltons) for the various formulations are 113 ppm Si for 0.5%:4.0%; 127 ppm for 1.0%:1.0%; and 171 ppm for 1.0%:2.0%. The clear superiority of the 1%:2.0% formulation in Table 6 is now evident.

Example 6

The ECF pulp of Example 1 used for peroxide/oxygen bleaching was treated with an acidic chlorine dioxide stage while the TCF pulp was acid-washed. Calcium that was bound to the pulps dissolved in the acidic solutions and was washed out. Six effluents from peroxide/oxygen bleaching of ECF pulps and

- 19 -

five effluents from TCF pulps were collected and divided in two. Calcium chloride was added to one half of each effluent to give a concentration of 50 ppm Ca^{2+} in solution. Smaller volumes of the straight and calcium-enriched effluents were adjusted to pH values of 9.0 and 10.0, than one inch square strips of 20-mesh stainless steel were placed in each solution or slurry. All of the selected effluents contained both epsom salt and sodium silicate. There was no magnesium silicate precipitate at either pH value, but there were calcium-magnesium silicate precipitates in most of the eleven effluents that were enriched with calcium chloride.

Each metal strip weighed about 1.6 grams initially and, surprisingly, none of them gained any weight when placed in any of the magnesium silicate solutions or the calcium-magnesium silicate slurries for more than 96 hours at room temperature (about 20°C). When taken from the solution or slurry, each strip weighed within 2 milligrams of its initial weight after washing and air-drying. This confirms that calcium silicates adhere to metals while calcium-magnesium and magnesium silicates do not.

Unbleached pulps are normally not acid-washed or treated with chelating-agents before O_2 delignification. Therefore, pulps normally enter an oxygen delignification stage with higher concentrations of calcium than that of pulps entering a peroxide/oxygen stage. However, if 1% epsom salt and 2% sodium silicate is added, there would be enough magnesium cations to chemisorb most of the dissociated silanol groups at pH values less than 11. Since magnesium cations are preferentially chemisorbed over calcium cations, any potential precipitate would be rich in magnesium. It is unlikely that such precipitates would scale the oxygen washers, where the pulp is washed after oxygen delignification. Scaling is unlikely at the high pH values of the black liquor (i.e., washed liquor from the unbleached pulp) evaporators, which are used to evaporate moisture after washing and before burning the now concentrated black liquor in a kraft recovery furnace. The likely scenario is that the calcium-magnesium silicate will pass through the kraft recovery furnace and be removed with the dregs at the green liquor clarifier. (Green liquor is the viscous fluid removed from the bottom of the recovery furnace and is made up primarily of inorganic compounds, such as sodium sulfide and sodium carbonate.) After removal, green liquor is diluted and insoluble materials (i.e., dregs) are separated by sedimentation. A high rate of sedimentation is observed for these calcium-magnesium silicate particles.

- 20 -

The effect of the magnesium sulfate/sodium silicate combination on oxygen delignification is demonstrated below in Table 7. Two-stage oxygen delignification of a 41 kappa number kraft pulp was simulated by adding 2% NaOH on pulp and 0.72 MPa of oxygen at 12% consistency and 90°C for 30 minutes, followed by a second NaOH injection (1.0% NaOH on pulp), restoration of oxygen pressure, and 30 minutes of additional retention. The standard oxygen included 0.5% epsom salt on pulp added during the preheat stage, i.e., before all other chemicals. When silicate was used, 1% Epsom salt on pulp was added at the preheat stage and 2% sodium silicate was added along with the first sodium hydroxide injection. Silicate additions significantly improved delignification selectivity (kappa number versus viscosity). Pulp brightness is also increased.

Table 7

Effect of Silicate Addition on Kappa Number and Viscosity After O₂ Delignification

	Standard Oxygen	O ₂ with Silicate
MgSO ₄ 7H ₂ O, % on pulp	0.5	1.0
Silicate, % on pulp	0	2.0
end pH	11.0	11.6
Brightness, %	28.2	30.8
Kappa No.	20.4	20.0
Viscosity, cP	21.2	24.7

¹Laboratory pulp made from 5 kg of chips, kappa number 41, viscosity 35 cP and screened yield of 47.8%

The improvement in viscosity is significant because viscosity is lowered further by most delignification and brightening stages, including P/O stages. If the viscosity is lowered below 10-12 cP (DP ~ 1000) then the strength values of paper made from the pulp decline dramatically.

Although illustrated and described herein with reference to certain specific embodiments and examples, the present invention is nevertheless not intended to be limited to the details shown. Rather, the claims should be read to include various modifications within the scope and range of equivalents of the claims, without departing from the spirit of the invention.

- 21 -

What is Claimed is:

1 1. A combination of additives for use in a brightening stage of
2 pulps containing less than 18% lignin, said combination comprising: an aqueous
3 sodium silicate solution; an alkali agent added in an amount sufficient to maintain
4 a pH of said solution at least about 8; and a magnesium compound which
5 dissociates in said solution to form $\text{Mg}(\text{OH})^+$ cations, wherein said magnesium
6 compound is added in an amount to achieve, along with any other dissociated
7 magnesium, an $\text{Mg}:\text{SiO}_2$ mass ratio of between about 1:46 to about 1:2.

1 2. A combination of additives in accordance with claim 1,
2 wherein said $\text{Mg}:\text{SiO}_2$ mass ratio is between about 1:15 to about 1:3.

1 3. A combination of additives in accordance with claim 1,
2 wherein said alkali agent is added in an amount sufficient to maintain the pH of
3 said solution within the range of from about 8 to about 12.

1 4. A combination of additives in accordance with claim 1,
2 wherein said magnesium compound is magnesium sulfate, added as MgSO_4 or
3 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

1 5. A combination of additives in accordance with claim 1,
2 wherein:

3 said aqueous sodium silicate solution is added in an amount to
4 achieve a concentration of from about 0.14% to about 1.4% SiO_2 on pulp; and

5 said magnesium compound is added in an amount to achieve a
6 concentration of from about 0.01% to about 0.2% Mg on pulp.

1 6. A combination of additives in accordance with claim 5,
2 wherein:

3 said aqueous sodium silicate solution is added in an amount to
4 achieve a concentration of from about 0.28% to about 1.12% SiO_2 on pulp; and

5 said magnesium compound is added in an amount to achieve a
6 concentration of from about 0.02% to about 0.2% Mg on pulp.

- 22 -

1 7. A combination of additives in accordance with claim 1,
2 wherein said alkali agent is selected from the group consisting of at least one of
3 NaOH, Na₂O, MgO, Mg(OH)₂, K₂O, KOH, CaO, and Ca(OH)₂.

1 8. A combination of additives in accordance with claim 1,
2 wherein said magnesium compound is selected from the group consisting of at
3 least one of MgO, MgCl₂, Mg(OH)₂ and MgNO₃.

1 9. An aqueous composition for use in a brightening stage of
2 pulps comprising:

3 pulp containing less than 18% lignin;

4 an aqueous sodium silicate solution;

5 an alkali agent added in an amount sufficient to maintain the pH at
6 least about 8; and

7 a magnesium compound which dissociates in said solution to form
8 Mg(OH)⁺ cations, wherein said magnesium compound is added in an amount to
9 achieve, along with any other dissociated magnesium, an Mg:SiO₂ mass ratio of
10 between about 1:46 to about 1:2.

1 10. An aqueous composition in accordance with claim 9, wherein
2 said Mg:SiO₂ mass ratio is between about 1:15 to about 1:3.

1 11. An aqueous composition in accordance with claim 9, wherein
2 said alkali agent is added in an amount sufficient to maintain the pH of said
3 solution within the range of from about 8 to about 12.

1 12. An aqueous composition in accordance with claim 9, wherein
2 said magnesium compound is magnesium sulfate, added as MgSO₄ or
3 MgSO₄·7H₂O.

1 13. An aqueous composition in accordance with claim 9, wherein:
2 said aqueous sodium silicate solution is added in an amount to
3 achieve a concentration of from about 0.14% to about 1.4% SiO₂ on pulp; and

4 said magnesium compound is added in an amount to achieve a
5 concentration of from about 0.01% to about 0.2% Mg on pulp.

1 14. An aqueous composition in accordance with claim 13,
2 wherein:

- 23 -

3 said aqueous sodium silicate solution is added in an amount to
4 achieve a concentration of from about 0.28% to about 1.12% SiO₂ on pulp; and

5 said magnesium compound is added in an amount to achieve a
6 concentration of from about 0.02% to about 0.2% Mg on pulp.

1 15. An aqueous composition in accordance with claim 9, wherein
2 said alkali agent is selected from the group consisting of at least one of NaOH,
3 Na₂O, MgO, Mg(OH)₂, K₂O, KOH, CaO and Ca(OH)₂.

1 16. An aqueous composition in accordance with claim 9, wherein
2 said magnesium compound is selected from the group consisting of at least one of
3 MgO, MgCl₂, Mg(OH)₂ and MgNO₃.

1 17. An aqueous composition in accordance with claim 9, wherein
2 said pulp contains less than 5% lignin.

1 18. An aqueous composition in accordance with claim 17,
2 wherein said pulp contains less than 2% lignin.

1 19. An aqueous composition in accordance with claim 9 further
2 comprising hydrogen peroxide.

1 20. A method for brightening pulp comprising the steps of:
2 mixing pulp containing less than 18% lignin with hydrogen
3 peroxide, an aqueous sodium silicate solution; an alkali agent added in an amount
4 sufficient to maintain the pH of said solution at least about 8; and a magnesium
5 compound which dissociates in said solution to form Mg(OH)⁺ cations, wherein
6 said magnesium compound is added in an amount to achieve, along with any other
7 dissociated magnesium, an Mg:SiO₂ mass ratio of between about 1:46 to about
8 1:2, to form a mixture; and

9 heating said mixture to allow said mixture to react to cause a portion
10 of said lignin to degrade.

1 21. A method in accordance with claim 20 further comprising
2 pressurizing said mixture with an oxygen-containing gas.

1 22. A method for delignifying and brightening pulp comprising
2 the steps of:

- 24 -

3 mixing pulp containing less than 18% lignin with an aqueous sodium
4 silicate solution; an alkali agent added in an amount sufficient to maintain the pH
5 of said solution at least about 8; and a magnesium compound which dissociates in
6 said solution to form $\text{Mg}(\text{OH})^+$ cations, wherein said magnesium compound is
7 added in an amount to achieve, along with any other dissociated magnesium, an
8 $\text{Mg}:\text{SiO}_2$ mass ratio of between about 1:46 to about 1:2, to form a mixture;

9 pressurizing said mixture with an oxygen-containing gas; and
10 heating said mixture to allow said mixture to react to cause a portion
11 of said lignin to degrade.

1 23. A method in accordance with claim 22 wherein the oxygen
2 partial pressure is in the range of between about 0.38 to about 1.48 MPa.

1 24. A method for brightening pulp containing transition metals
2 and less than 18% lignin, said method comprising the steps of:

3 forming a sodium silicate solution having a high percentage of high
4 molecular weight silicates by mixing sodium silicate and a magnesium compound
5 which dissociates in said solution to form $\text{Mg}(\text{OH})^+$ cations; and

6 adding said sodium silicate mixture to said pulp to adsorb at least a
7 portion of said transition metals.

1 25. A method of claim 24, wherein said sodium silicate mixture
2 has at least 25% of the silicates with molecular weight of at least 10,000 daltons.



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(54) Title: PEROXIDE, OXYGEN, AND PEROXIDE/OXYGEN BRIGHTENING OF CHEMICAL AND MIXED WASTE PULPS (57) Abstract <p>A composition and method for use in the peroxide, oxygen, or peroxide/oxygen stage of brightening pulps with less than 18 % lignin utilize a magnesium compound in a sodium silicate solution to form a higher percentage of high molecular weight silicates. Such high molecular weight silicates preferentially adsorb transition metal impurities which, if left in solution, would tend to decompose hydrogen peroxide and organic peroxides. Hydrogen peroxide is added to peroxide and peroxide/oxygen stages, while it is generated, along with organic peroxides, during an oxygen stage. Decomposition decreases the amount of peroxide that actually reacts with lignin and generates free radicals that attack the desired product, carbohydrate fibers. The high molecular weight silicates can be formed by using any magnesium compound which dissociates to form $Mg(OH)^+$ cations, which in turn cause a silicate polymerization reaction. The formation of $Mg(OH)^+$ cations from magnesium compounds occurs most readily over a pH range of at least about 8 and preferably between about 8 and about 12. The magnesium compound is added in an amount to achieve an $Mg:SiO_2$ mass ratio of between about 1:46 to about 1:2, and preferably between about 1:15 to about 1:3.</p>		

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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